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OLIVINE

BY

G. RICHARDS GWINN

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

OLIVINE[1/]

By G. Richards Gwinn[2/]

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INTRODUCTION

The mineral olivine, though known to mineralogists for many years, was of little commercial value in the United States before 1933. It was first described in 1790 by Johann Gottlieb Werner, who named it "olivine" in allusion to its olive-green color.

Commercial olivine first attracted attention because of its refractory properties. Further research has developed methods of extracting the magnesia content for the production of various magnesium compounds. Experimental and pilot-plant work also are in progress to make olivine available as a low-cost raw material for the production of magnesium metal.

1/ The Bureau of Mines will welcome reprinting of this paper provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7239."

2/ Nonmetal Economics Division, Bureau of Mines.

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DESCRIPTION AND OCCURRENCE

The minerals of the olivine group, all of which crystallize in the orthorhombic system, are orthosilicates with the general formula $R_2''SiO_4$, in which R'' may be Mg, Fe, or Mn. They consist of two end members - forsterite, Mg_2SiO_4, and fayalite, Fe_2SiO_4 - and the intermediate isomorphous mixture, olivine $(Mg,Fe)_2SiO_4$, of which dunite, a monomineralic rock of the peridotite class, is composed. There are also tephroite, Mn_2SiO_4; glaucochroite, $CaMnSiO_4$; and the double salt, monticellite, $CaMgSiO_4$, but these are rare minerals. Dunite and its alteration products, serpenting and talc, are the chief sources of raw material used in the production of forsterite refractories and, more recently, other magnesium compounds.

Forsterite (Mg_2SiO_4), the magnesian end member of the olivine group, is rarely found alone. Its color is white, greenish, or yellow; hardness, 6 to 7; and specific gravity, 3.21 to 3.33. Optically, it is a biaxial positive mineral with a large axial angle, and a mean index of refraction of 1.655 to 1.660. Cleavage is imperfect, and irregular fractures are common.

Fayalite (Fe_2SiO_4), the iron end member of the olivine group, like forsterite, is rarely found alone. It is usually light greenish yellow but may be brown or black, owing to oxidation; hardness, 6.5; and specific gravity, 4.1. Optically, it is a biaxial mineral with a negative sign. The axial angle is of medium size, and its mean index of refraction is 1.877.

Olivine $(Mg,Fe)_2SiO_4$, usually occurs in granular masses or disseminated crystals and grains. Its color is yellowish to olive green, but, owing to oxidation of the iron, may be brown, grayish, or red; hardness, 6.5 to 7; and specific gravity, 3.27 to 3.37. Optically, it is a biaxial mineral and usually has a positive sign, but may be negative due to an increase in the iron content. The axial angle is large, and the mean index of refraction is 1.667 to 1.690.

Occurrence. - For the most part, forsterite is limited to metamorphic limestones. Fayalite is found in granite pegmatites, rhyolitic obsidians, and some ores. Olivine is abundant as a rock-forming mineral in subsilicic igneous rocks, particularly the peridotites, which have been named for the olivine they contain. It also occurs in tuffs, volcanic bombs, and meteorites. Clear, transparent olivine is used as a gem stone under the names peridot, evening emerald, and chrysolite.

DUNITE

Dunite and its alteration products are the rocks that contain olivine in commercial quantities; therefore, a description of them and a summary of the geologic occurrence of the largest deposits in the United States are given here.

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Description. - Dunite consists essentially of even-grained crystalline olivine with minor amounts of chromite disseminated through the mass as well as an occasional grain of pyroxene. The original dunite rock was first described and named by Ferdinand von Hockstetter in 1859 from its occurrence on Dun Mountain, 6 miles southeast of Nelson, New Zealand. The impurities in dunite that lower its refractory properties, with the exception of the iron, which is in solid solution in the olivine, are products of alteration of olivine by weathering, serpentinization, steatitization or alteration to talc, and alteration to chlorite.

Alteration. - Dunite weathers rapidly under the influence of oxygen, moisture, and carbon dioxide of the air. The first traces of alteration are characterized by the yellowish brown color assumed by the rock owing to separation of a portion of the iron as hematite, goethite, or the hydrous oxide, limonite. As weathering increases, the rock becomes more friable and finally crumbles to an ocherous mass traversed in an irregular manner by veins of chalcedony. Serpentinization of the dunite, which occurs below the zone of weathering, is essentially a process of hydration during which a portion of the iron separates out as secondary magnetite. Swelling and fracturing of the dunite mass is also a result of this alteration. Steatitization or alteration to talc results from the action of late hydrothermal solutions on the serpentine formed by the first alteration of dunite. Alteration to chlorite involves the loss of magnesia and the addition of alumina and water. Analyses of dunite show a small amount of aluminum but not enough to permit the alteration of the rock to chlorite. Therefore, it must be assumed that the aluminous solutions have come from the rocks surrounding the dunite mass.

Geology. - Large deposits of dunite are found in the mountains of western North Carolina and Georgia and the Puget Sound region of Washington. The deposits in North Carolina and Georgia are part of a series of peridotite masses that cut the pre-Cambrian gneisses and schists of eastern North America. In Georgia and North Carolina these masses are of comparatively fresh dunite, although locally they may be altered to serpentine and talc. In Virginia, Maryland, and Pennsylvania they are composed chiefly of serpentine and soapstone. They continue north and east through the New England States, and outcrops of unaltered dunite reappear in the Gaspé Peninsula and Newfoundland. Chromite is a constant accessory and occurs either as disseminated grains or as pockets, which in a few places have been large enough to work commercially.

The two largest deposits of dunite in Washington are found in the Twin Sisters mountain region, about 10 miles southwest of Mount Baker and approximately 90 miles northwest of Seattle, and on the southeast corner of Cypress Island about 80 miles northwest of Seattle. They have been intruded into altered volcanics, phyllites, and schists of possibly upper Jurassic age.

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Dunite outcrops in the Twin Sisters area as an elliptical mass 10 miles long by 5 or 6 miles wide and at elevations of 3,000 to 6,000 feet above sea level. The region is rugged and accessible only by mountain trails. This is the largest and least altered body of its kind known in the United States and consists essentially of dunite, saxonite, and the ubiquitous accessory chromite. Saxonite is a peridotite consisting of olivine and an orthorhombic pyroxene. In this locality the pyroxene is enstatite, a magnesian silicate. Alteration of the Twin Sisters dunite is confined to weathering, as there is no evidence of serpentinization, steatitization, or alteration to chlorite.

Cypress Island dunite forms a symmetrical dome called "Olivine Hill," at the southeast end of the Island, which rises to about 600 feet at the center and covers an area of about one-half by two-thirds of a mile. A large portion of this dunite has been altered by weathering and serpentinization. The importance of this deposit lies in its large tonnage of refractory olivine at tidewater accessible to cheap water transportation.

RESERVES

Estimated reserves of olivine in these deposits, averaging 45 to 49 percent magnesia, are enormous. These are given as 230 million tons in the North Carolina and Georgia deposits, 50 million tons on Cypress Island, and although no figures have been published on the Twin Sisters region, T. P. Thayer of the Federal Geological Survey states that it is in the order of millions of tons.

USES

The principal uses for olivine have been in the refractory field, where it is the chief raw material in the manufacture of forsterite refractories. A minor use is for production of magnesium chemicals.

Forsterite bricks are used in the roofs of copper holding and copper reverberatory smelting furnaces and in the top portion of the lining of converters for blowing scrap brass. In the steel industry, they give satisfactory service in the end wall, bridge wall, and ports of open-hearth furnaces. They are also being used as linings in portland-cement and dolomite rotary kilns, in walls and roofs of ceramic kilns, and as a source of material for furnace repair in all of the above-mentioned industries. An olivine mortar developed and patented by Harvey and Birch is of special importance to users of olivine refractories. It not only joins forsterite bricks, but magnesite, chromite, and many other refractories as well.

A recent and possibly the first use of olivine as raw material for the production of magnesium chemicals is in a plant operated by the Olivine Products Corporation of Webster, N. C. The process consists essentially of

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digesting crushed olivine in sulfuric acid, separating the iron, and crystallizing [illegible] magnesium sulfate from solution. The markets for these salts are the local tanneries, rayon, paper, textile and pharmaceutical trades. The fertilizer industry also provides an outlet for this product as an inexpensive source of soluble magnesium.

In the course of laboratory and plant tests on the refractory properties of Pacific Northwest olivine, it has been shown that olivine can be used locally as foundry or blast sand. The high melting temperature, a hardness similar to quartz, no sudden changes in volume due to mineral inversion, and the comparatively low coefficient of expansion of olivine are its desirable attributes as a foundry sand.

Experimental work is in progress to determine the potentialities of olivine as an ore of magnesium. With the exception of brucite, olivine contains more magnesium than any other common mineral - 27 to 30 percent. However, the chemical processing industry has felt that the cost of processing silicates is an economic barrier to their utilization, particularly when the more reactive carbonates, oxides, or salts are available. The processing problem involves breaking down the silicate structure and removal of the gelatinous or colloidal precipitates of iron and silicon hydrates, which are products of the leaching process.

It is felt that these difficulties can be overcome because olivine, unlike most silicates, is readily attacked by acids without resort to fusion to break down the silicate structure, and the colloidal and gelatinous precipitates can be disposed of by neutralizing the reacted mass before leaching. Minor impurities that will tend to impede production of magnesium from dunite are chromite, nickel silicates, and manganese oxide. Nickel and chromite are potential by-products, and manganese can be left in to advantage. The experimental methods in progress are: (1) The conversion of olivine to magnesium chloride by leaching with hydrochloric acid, and the use of this chloride as electrolytic cell feed to produce the oxide; and (2) the production of magnesium sulfate by a sulfuric acid leach and the subsequent calcination of this sulfate to the oxide.

Although demands for magnesium in the armament program have greatly exceeded normal requirements and have placed new emphasis on sources of this material, olivine originally was considered as a raw material that might stand on its own merits in peacetime economy.

HISTORY OF FORSTERITE REFRACTORIES

A study of the magnesium silicates, olivine and its alteration products serpentine and talc, for use as refractories has culminated in the successful

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development of a refractory in which forsterite is the principal constituent. Independent studies of these silicates in Europe and the United States reached identical conclusions, although the European studies antedated the work in this country by about 10 years.

Jakob (11)[3/] in 1924, was the first to suggest the use of forsterite as a refractory. He proposed that a mixture of serpentine, quartz, and magnesium sulfate be melted in an electric furnace to obtain refractory forsterite. Because of technical difficulties, this process is not industrially important.

The first experimental manufacture of forsterite products was started in 1925-6 by Goldschmidt (2) and Knudson in Norway using talc and magnesium oxide. During the progress of this work it was found that serpentine and magnesium oxide could also be combined to form forsterite, and that forsterite products of excellent properties could be made by such a process. The industrial use of these refractories from 1928 to 1931 was largely developed in Germany. In 1933 Goldschmidt and Siedentopf (3) were granted a United States patent covering mixtures of olivine and magnesium oxide or magnesium chlirido, or both, heat treated to produce forsterite. The granting of this patent marked the beginning of extended research in this country, which has produced forsterite refractories of commercial grade. Almost all of these have been made from magnesia, olivine, serpentine, and talc.

PROPERTIES OF FORSTERITE REFRACTORIES

Forsterite refractories fired and unfired are made of olivine-bearing rock that may contain 85 percent of forsterite. The fired refractories also contain magnesia and chromite added during the manufacturing process to develop additional forsterite from the alteration products, talc and serpentine, that occur with olivine. Without the addition of these conversion agents, talc and serpentine provide a low melting bond that would cause failure of the refractory at relatively low temperature under load. Following is a list of the properties of fired forsterite refractories (6):

Chemical composition:	SiO_2, 31.7 percent; Al_2O_3, 1.1; FeO plus Fe_2O_3 (as FeO), 6.4; CaO, 2.8; MgO, 57.2; Cr_2O_3, 0.1.
Specific gravity:	Brick weighs about 155 lb. per cu. ft. and has a bulk specific gravity of 2.5. This is less than magnesite and chrome brick and higher than silica.

3/ Numbers in parentheses refer to bibliography at end of text.

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Porosity:	Range of apparent porosity, 24 to 28 percent.
Density:	3.36 grams per cubic centimeter.
Refractoriness:	Above cone 38 (1,835° C.) considerably more refractory than silica brick, at cone 32 (1,700° C.).
Volume stability:	Maximum of 0.5 percent linear shrinkage when heated to 1,650° C. for 5 hours.
Strength under load:	Cold crushing strength about 2,500 lb. per sq. in. In A.S.T.M. hot load tests withstood load of 25 lb. per sq. in.
Slag resistance:	Equal to chrome brick and better than magnesite brick.
Spalling resistance:	More resistant to spalling than magnesite brick, but below that of the average fire-clay brick.
Thermal conductivity:	Lower than that of silica brick at high temperature.
Thermal expansion:	Expansion rate is uniform and of the same order but lower than that of magnesite brick.

Unfired refractories consist of crushed olivine and a cold-setting bonding agent that will produce a commercial unfired forsterite refractory. The critical factors in the production of this type of refractory are the proper grinding and screening of the olivine and the use of a bonding agent that will not lower the pyrometric cone value of the finished product.

After extensive research on bonding agents at the Engineering Experiment Station of North Carolina State College at Raleigh, N. C., Greaves-Walker and Stone recommend the following mixes and bonding agents (4):

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Calcine: 88.29 percent of olivine to pass at least 6 mesh.

11.71 percent of Linifrit[1] to pass at least 35 mesh. Calcine at 3,000° F. or above.

Mix No. 1: 92.5 percent of above calcine.

7.41 percent of Lumnite[2] cement.

Mix No. 2: 99.01 percent of above calcine.

0.99 percent of "O Brand"[3] sodium silicate (based on anhydrous solid).

1/ Linifrit - high-lime magnesite.
2/ Lumnite cement - a cement containing a high aluminum oxide content.
3/ "O Brand" sodium silicate - a sodium silicate composed of 29.3 percent SiO_2, 9.1 percent Na_2O, and 61.6 percent H_2O.

There follows a list of the properties of unfired forsterite refractories:

Chemical composition:	SiO_2, 34.1 percent; Al_2O_3, 4.40; Fe_2O_3, 7.70; CaO, 4.90; MgO, 47.90; alkalies, 0.04.
Dry bulk specific gravity:	2.24-2.26
Fired bulk specific gravity:	2.26-2.30
Percent of porosity at cone 19 (1,520° C.):	1.0-1.7
Unfired compressive strength:	1,500-3,500 lb. per sq. in.
No failure in temperature gradient	
Pyrometric cone equivalent cone 36 plus (1,810° C.)	

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PRODUCTION

Production of olivine for industrial uses in the United States began in North Carolina on a very small scale in 1930, and production figures for 1932 to 1940 were estimated. Beginning with 1941, the Bureau of Mines conducted a canvass of individual producers. Production figures for 1932 to 1942 follow:

Production of olivine in the United States, 1932-41

Year	Short tons	Year	Short tons
1932	720	1937	4,000
1933	1,500	1938	2,800
1934	3,000	1939	3,000
1935	6,000	1940	3,000
1936	5,000	1941	4,828

Prices for olivine quoted in the Engineering and Mining Journal Metal and Mineral Markets of December 1942 are $5 to $7 a short ton for crude, $17 a ton ground to 200 mesh, and $12 a ton for 20 mesh to dust, all f.o.b. North Carolina.

FOREIGN DEPOSITS, AND PRODUCTION

Large deposits of olivine-bearing rocks outcrop in Norway, Italy, U.S.S.R., Germany, Japan, New Caledonia, New Zealand, and Africa. The large chromite deposits of New Caledonia and Africa are associated with dunite, as are the platinum mines in the Ural Mountains of the U.S.S.R. The diamond mines of southwest Africa are in volcanic rocks called "kimberlite," a serpentinized rock derived from peridotite.

Production of forsterite refractories in Europe on a commercial scale from raw material imported from Norway began in Germany in 1928. The process consisted of transforming olivine rock into a mixture of forsterite and magnesium ferrite. The successful use in England in 1936-7 of forsterite bricks in forging and reheating furnaces of steel works served as an impetus to open new markets in several European countries. Synthetic forsterite was produced in Germany in 1937 from a mixture of serpentine and magnesium oxide. This process made it possible to produce forsterite refractories without importing raw material. Reports have been received that from 1938 to 1940 highly refractory material was produced from dunite in the Ural Mountains of the U.S.S.R. and the serpentines of Italy. In 1940 the Japanese produced and patented a basic refractory under the trade name "Magnite," whose main constituent is forsterite. It is used in many steel plants as a substitute for chrome or magnesite brick.

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There follows a partial list of papers and publications that discuss the uses of olivine in the industrial field. Most of these are available in local college, engineering, or public libraries.

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LIST OF BUYERS AND PRODUCERS OF OLIVINE

Producers

MARYLAND:
Clinchfield Sand & Feldspar Corporation, 618 Mercantile Trust Bldg., Baltimore.
NEW JERSEY:
D. C. Wysor, 136 Brookfield Ave., Ridgewood.
NORTH CAROLINA:
United Feldspar & Minerals Corporation, Spruce Pine, N. C.
Operations at:
Cogdill and Garnet mines, Balsam.
Minpro plant, Spruce Pine.
Green Mountain olivine mine, Green Mountain.
Chestnut Mountain olivine mine, Micaville.
Madison County olivine mine, Marshall.
PENNSYLVANIA:
Harbison-Walker Mining Co., Farmer's Bank Bldg., Pittsburgh.

Buyers

CANADA:
Algoma Steel Co., Sault St. Marie.
KENTUCKY:
Corhart Refractories Co., Louisville.
NEW JERSEY:
Refractory Mica Products, Inc., Irvington.
W. Ames & Co., Jersey City.
Federal Seaboard Terra Cotta Corporation, Perth Amboy.
OHIO:
Otis Steel Co., Cleveland.
American Rolling Mill Co., Middletown.
Wheeling Steel Corporation, Steubenville.
PENNSYLVANIA:
Bethlehem Steel Corporation, Bethlehem.
American Steel & Wire Co., Donora.
Carnegie-Illinois Steel Corporation, Farrell.
WEST VIRGINIA:
Wheeling Steel Corporation, Benwood.
Weirton Steel Co., Weirton.

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